

**SPACE PLASMA ION PROCESSING OF ILMENITE IN THE LUNAR SOIL: INSIGHTS FROM IN-SITU TEM ION IRRADIATION EXPERIMENTS.** R. Christoffersen<sup>1</sup> and L. P. Keller<sup>2</sup>, <sup>1</sup>SAIC, 2450 NASA Parkway, Houston, TX 77058 ([roy.christoffersen1@jsc.nasa.gov](mailto:roy.christoffersen1@jsc.nasa.gov)), <sup>2</sup>Mail Code KR, ARES Directorate, NASA Johnson Space Center, Houston, TX 77058.

**Introduction:** Space weathering on the moon and asteroids results largely from the alteration of the outer surfaces of regolith grains by the combined effects of solar ion irradiation and other processes that include deposition of impact or sputter-derived vapors. Although no longer considered the sole driver of space weathering, solar ion irradiation remains a key part of the space weathering puzzle, and quantitative data on its effects on regolith minerals are still in short supply. For the lunar regolith, previous transmission electron microscope (TEM) studies performed by ourselves [1] and others [2] have uncovered altered rims on ilmenite ( $\text{FeTiO}_3$ ) grains that point to this phase as a unique “witness plate” for unraveling nanoscale space weathering processes. Most notably, the radiation processed portions of these ilmenite rims consistently have a crystalline structure, in contrast to radiation damaged rims on regolith silicates that are characteristically amorphous. While this has tended to support informal designation of ilmenite as a “radiation resistant” regolith mineral, there are to date no experimental data that directly and quantitatively compare ilmenite’s response to ion radiation relative to lunar silicates. Such data are needed because the radiation processed rims on ilmenite grains, although crystalline, are microstructurally and chemically complex, and exhibit changes linked to the formation of nanophase Fe metal, a key space weathering process. We report here the first ion radiation processing study of ilmenite performed by *in-situ* means using the Intermediate Voltage Electron Microscope-Tandem Irradiation facility (IVEM-Tandem) at Argonne National Laboratory. The capability of this facility for performing real time TEM observations of samples concurrent with ion irradiation makes it uniquely suited for studying the dose-dependence of amorphization and other changes in irradiated samples.

**Experimental Approach:** The irradiations were performed on an ion milled thin section of lunar basalt 70215. This is a high-Ti mare basalt that contains 13 modal percent ilmenite grains ranging from  $50\mu\text{m}$  up to 3 mm in size [3]. The other major phases are clinopyroxene (58%), plagioclase (18%), and olivine (6%) [3]. The ilmenite has 10-16 atom % substitution of Mg for Fe but is otherwise a fully-reduced end-member ilmenite (i.e., no  $\text{Fe}^{3+}$  substitution). Our experiments followed standard IVEM-Tandem methodology in which ion-milled samples are irradiated by a ~2 mm-diameter

ion beam introduced at  $30^\circ$  off-angle to the optic axis of a modified 300 kV Hitachi H9000 NAR high-resolution TEM. The overall experimental geometry amounts to watching changes in thin crystalline regions of grains as they receive ion radiation roughly co-axial with the electron beam. Although the 100 keV to 1 MeV total ion energy range of the Tandem Accelerator does not allow for direct duplication of typical ion energies in either the solar wind, Solar Cosmic Rays, or Galactic Cosmic Rays, it does allow for selection of ions masses and energies with high amorphization potential by nuclear stopping mechanisms. We selected 1 MeV Kr ions for the irradiations for this reason as well as the fact that they had been used in a number of previous studies on silicate and sulfide amorphization [4,5,6,7]. Modeling of energy deposition, ion range and atomic displacements in the samples was performed using the most recent version of the TRIM (TRansport of Ions in Matter) code [8].

**Ilmenite Irradiation Results:** Changes in the ilmenite grains during irradiation were monitored in real-time by selected-area electron diffraction and bright-field imaging assisted by video recording with a TV camera. Typically a suitably thin single grain in a symmetrical zone axis diffraction orientation was monitored while the ion beam was active. If notable changes in this reference grain were observed, irradiation was temporarily blanked while observations were documented for other grains across the sample. This included checks on progressive changes in the silicate phases in the sample, with particular emphasis on the constituent pyroxene. A summary of the TEM diffraction and imaging results as a function of increasing ion dose is provided in Table 1.

**Discussion:** The ilmenite exhibited complex and progressive nanostructural changes with increasing ion dose, but overall retained the average structure of a single-crystal up to the maximum practical ion dose of  $9 \times 10^{15}$  ions/ $\text{cm}^2$ . In contrast, pyroxene in the same sample showed the abrupt onset of complete amorphization at close to an order of magnitude lower dose. The radiation-induced amorphization of the pyroxene is symptomatic of the “critical amorphization dose” behavior observed in many silicates [4,5,6,7]. This is characteristic of more complex, lower-symmetry crystal structures that easily accumulate anti-site defects and short range disorder during irradiation, eventually

Table 1. *In-situ* ion irradiation TEM observations

Kr ion dose (ion/cm <sup>2</sup> )	$1 \times 10^{14}$	$5 \times 10^{14}$	$1 \times 10^{15}$	$7 \times 10^{15} \gg 8 \times 10^{15} \gg 9 \times 10^{15}$ (final dose)	
Equivalent solar wind He (4 keV) dose (ions/cm <sup>2</sup> )	$4 \times 10^{15}$	$2 \times 10^{16}$	$4 \times 10^{16}$	$2.8 \times 10^{17} \gg 3.2 \times 10^{17} \gg 3.6 \times 10^{17}$ (final dose)	
Ilmenite	Diffraction	no change (relative to starting material)	No change - strong discrete single-crystal pattern	Faint complex (non-circular) diffuse scattering intensity between strong main reflections	
	Imaging	no change	Thinner outer edge of ion-milled grains completely amorphous, thicker regions show faint speckled/mottled strain contrast on 10-20 nm scale	Mottled BF contrast accentuated – but SAD indicates single-crystal structure	
Pyroxene	Diffraction	no change	no change	Discrete reflections replaced by diffuse ring pattern – completely amorphous at $1 \times 10^{15}$ and above	
	Imaging	no change	no change		

triggering a rapid first-order-like transformation to the glassy state. In ilmenite the structural changes in response to irradiation are clearly more progressive, occurring over a broader dose range. For the thin edges of the ion-milled ilmenite grains the formation of completely amorphized material cannot be attributed to any differences in ion range/deposited collision energy relative to thicker crystal regions, because the ion energy/ion range is too high. The amorphous edges are more likely artifacts promoted by pre-existing partially amorphous material from the ion milling process. For the thicker regions of crystal, however, the data do indicate the formation, with increasing ion dose, of what appear to be nano-scale regions of amorphous structure inside a structurally continuous single-crystal matrix. The presence of diffuse scattering intensity more complex than simple ring patterns in the sample at lower doses (see Table 1), suggest that there are intermediate structural stages in the formation of these regions. At ion doses higher than practical for the IVEM-Tandem facility it is possible that the nano-scale amorphous regions may grow sufficiently to result in complete amorphization of the ilmenite. It is also possible, however, that the microstructure we observe represent a near steady-state configuration.

**Implications for lunar regolith ilmenite.** Using TRIM, the Kr ion doses in our experiments were converted to equivalent doses for solar wind He needed to produce the same level of deposited nuclear collision energy per volume in the sample (Table 1). The final equivalent He dose of our experiments is quite close to previous estimates we have made for solar wind He in lunar grains [1]. Our experiments therefore reasonably

simulate the total amount of nuclear collision damage that ilmenite grains could receive during their residence time on the lunar surface. The experimental damage level is sufficient to produce visible microstructural changes but no appreciable loss of the long range atomic order needed to produce a single-crystal electron diffraction pattern. This matches, at least broadly, what is observed in the radiation processed rims in lunar ilmenites [1]. However, other important chemical and microstructural details of the lunar ilmenites, such as Fe segregation and reduction, and Ti-oxide precipitation [1], were not observed in our experiments. This may indicate that implantation of more chemically active solar wind H, possibly combined with some longer term thermal processing, is uniquely required to produce the changes in the lunar ilmenite rims.

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